Dibromine monoxide, Br_2O: the rotational spectrum and molecular properties

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Abstract

The rotational spectra of $^{79}Br_2O$, $^{79}BrO^{81}Br$, and $^{81}Br_2O$ in their ground vibrational states as well as $^{79}BrO^{81}Br$ in its $v_2 = 1$ state have been studied in selected regions bet wccn 90 and 523 GHz. Transitions involving a large range of quantum numbers, $6 < J \leq 123$ and $0 \leq K_a \leq 12$, have been observed permitting precise rotational and a large set of centrifugal distortion constants to be determined. All isotopic species as well as the excited slate data were fit simultaneously. Ground-state effective and average structural parameters as well as an estimate of the equilibrium structure have been derived. The quartic distortion constants were used for a calculation of the harmonic force field. The complete quadrupole tensor has been determined. Its diagonal ization reveals a largel y covalent BrO bond with little n-bonding. '1 'he derived properties of Br_2O arc compared with those of related compounds such as Cl_2O, 1 IOBr, and HOCl.

1. IN'I'RODUCTION

Few bromine oxides arc known, mainly because they arc unstable at mom temperature. Most of the limited spectroscopic and structural investigations were carried out in the solid state, "[2] Dibromine monoxide, Br_2O, is comparatively well characterized. It was obtained in low yields by Zintl and Ricnäcker more than sixty years ago by passing Br_2 over 1 IgO as a not specified bromine oxide contaminated with unreacted bromine.[3] Using a solution of Br_2 in CCl_4, Brenschede and Schumacher obtained higher yields dissolved in CCl_4 and identified it.[4] Pure Br_2O was synthesized for the first time by Schwarz and Wiele as a decomposition product of a light yellow bromine oxide described as bromine dioxide.[5]

More recently, the Raman spectrum of solid Br_2O at 77 K was recorded by Campbell *et al.* including $^{16/18}O$ isotopic shifts for the stretching fundamentals.[6] The symmetric stretching vibration ν_1[7] or both stretching nlodes[8,9] were observed in Ar[7,8] or N_2 matrices[9] along with $^{16/18}O$ isotopic shifts. The structure of Br_2O in the solid phase was studied by EXAFS[9] (*E*xtended X-ray Absorption *F*ine *S*tructure) and very recently by single crystal X-ray diffraction.[10]

Very recently wc have given a preliminary account on the investigations of the rotational spectra of Br_2O and OBrO.[11] These have been the first high resolution studies and the first structure determinations of bromine oxides in the gas phase other than BrO. in this article the spectra of the three main isotopic species of Br_2O and the fitting procedure arc described in detail together with the derived spectroscopic constants and molecular properties.

EXPERIMENTAL SECTION

(a) Synthesis of Br_2O. Br_2O was synthesized by passing Br_2 through a column of yellow HgO at room temperature. The products were flowed through the microwave absorption cell at total pressures of 2-5 Pa. Although the yields were low, in agreement with earlier work,[3] many transitions could be observed with no or little signal averaging, This method has been used for most of the investigations.

During our studies of OBrO[11] it was discovered that Br_2O could be more readily observed as a secondary product of the O + Br_2 reaction than as a product of the Br_2 + HgO reaction. Products of an oxygen discharge + Br_2 were condensed on the wall of the absorption cell at -250 K. OBrO was evolved at *ca.* 250 K. At -260-270 K with pumping speeds adjusted to maintain pressures in the 0.5-2 Pa range, the Br_2O spectra became quite prominent. No effort has been made to characterize the solid product.

(b) Spectrometer. Details of the spectrometer have been given elsewhere.[12] The measurements were made employing a 1 m long, double-path coolable glass cell. Phase-locked klystrons (Varian) were used as sources, either on fundamental frequency (*ca.* 9061 Hz) with a diode detector, or at third to fifth harmonic using harmonic generators and a liquid He-cooled InSb hot electron bolometer as detector. Most of the measurements were done in the 383-434 and 611-7 and in the 312-322 GHz regions. Additional measurements were done at *ca.* 90 GHz and around 522 GHz.

11. R1OS1JI ,TS

(a) Observed Spectra and Assignment. Br_2O is a near symmetric prolate rotor (K ≈ **-0.9966)** with its dipole moment along the b-axis. The initial bond length of Br_2O was estimated to be 184-.3 pm from a comparison of ClO and BrO bond lengths in Cl_2O,[13] HOCl,[14] and HOBr.[15] This value is in agreement with 185 (1) pm from Ref. 9.1 he initial bond angle was taken from that study: 112 (2)°. Quartic distortion constants were derived from a force field calculation using the vibrational data from Refs. 6 and 8.

in the412 to 434 GHz region studied first $^rR_4$, $^rR_5$, $^rQ_6$, $^rP_8$, and $^rP_9$ branches were predicted to be the strongest ones. Each branch was expected to have a characteristic quadrupole pattern which varied slowly with J. The observation of the $^rQ_6$ branch for al 1 three isotopomers near 412 GHz (see Fig. 1 for a detail of the $^{79}Br_2O$ branch) and several members of the $^rR_5$ and $^rP_8$ branches permitted the unambiguous J assignment and the determination of rotational and diagonal quartic centrifugal distortion constants. The observation and assignment of selected transitions was then straightforward.

Using estimates of the vibration rotation interaction constants for the $v_2 = 1$ state derived from Cl_2O,[13] it was possible to identify one transition each of the $^rP_8$ and $^rP_9$ branches for the $^{79}BrO^{81}Br$ isotopomer in the first excited bending mode in previously recorded spectra, Several other transitions were sought and found. No effort was made to assign other vibrational states ofthc mixed isotopomer or any excited state of the symmetric isotopomers. All rotational transitions used in the fits are in '1'able 1. The complete line list is available as supplementary material,

Both Br nuclei, ^{79}Br and ^{81}Br, have a spin of 3/2. Diagonal quadrupole coupling constants

were estimated using those of' Cl_2O[16] scaled by the ratio eQq(BrO)/eQq(ClO)[17,18] and considering the slight change in bond angle. It was assumed that the *z*-quadrupolar axes coincide with the XO bonds.

Because of the two different Br nuclei each rotational transition of $^{79}BrO^{81}Br$ consists of 16 strong quadrupole components with A $J = \Delta J$. Both $^{79}Br_2O$ and ^{8}111r20 have C_{2v} symmetry. Because of the spin-statistics levels with J odd or even are missing for transitions with $K_a + K_c$ *even* or odd, respectively, reducing the number of strong hyperfine components to 6 or 10 respectively (see Figs. 2 and 3).

Transitions with higher J and K_a quantum numbers, which were among the first assigned, appear mostly as characteristic triplets for the C_{2v} species (Figs. 1 and 2) and as triplets or quartets for the mixed isotopomer.

At low J the quadrupole the splittings are large and dominated by χ_{aa}.[19] They can be rather complex (SCC Fig. 3). Because χ_- (= $\chi_{bb} - \chi_{cc}$) is large and of the same sign as χ_{aa} the quadrupole splittings rapidly decrease with increasing J (*SCC* Fig. 1). At some intermediate J they are minimal and often unresolvable in the absence of other effects; this value of J increases with K_a. At even higher J the patterns spread out again because of the increasing effect of χ_- (see Fig. 2).[19] Sonic transitions with large quadrupole splittings are given in '1'able 11,

The *z*-quadrupole axes are expected to be close to the BrO bonds which are not aligned with a principle inertial axis. Therefore, the off-diagonal quadrupole coupling constant χ_{ab} is non-zero. Effects related to this constant occur as perturbations of the quadruple patterns of near-degenerate levels with $|\Delta J| \leq 2$, $|\Delta K_a| = 1$, and ΔK_c even. Among the observed transitions the effects of χ_{ab} are

particularly noticeable in the $^rR_4$ branch and the $^rR_5$, $J = 40$ transition of the mixed isotopomer because they would have unresolvable quadruple splittings in the absence of P_{ab}. In several cases complex patters were observed as shown in Fig. 4. These arc duc to interactions between levels with $\Delta J = 2$, $\Delta K_a = -1$ as shown in Fig. 5. The A.]=- 1 resonances occur at higher J. They have been observed only for $K_a = 4$-3 around J of 80 (SCC also Table 2). The near-degeneracies of such levels contribute most to the precise determination of χ_{ab}, but more subtle effects of χ_{ab} are widespread throughout the spectrum.

(b) Fitting of the Spectra. predictions and fittings were done with Pickett's program SPCAT and SPJU'1'20 Because of the two Br nuclei a symmetric coupling scheme was employed: $\mathbf{I}_1 + 1_2 = \mathrm{I}$, **1-1 J = F**. Spin statistics were taken into account for the t wo isotopomers with C_{2v} symmetry. Because J is not a "good" quantum number strong mixing can occur so that the assignment of an J value to a particular state is sometimes not obvious. in a number of cases, the small changes encountered in the course of the iterative fit would change the program's assignments during the fitting procedure. Particularl y in thc beginning, the resulting spectroscopic constants were substantial] y affected. 1 n order to minimize these problems each transition for which the fitting program made multiple assignments was entered with al l alternate assignments. A rejection criterion was chosen so that onc and onl y one assignments would be included for each iteration.

The uncertainties attributed to the lines were in general onc tenth of thc half-width; they were increased for lines with low signs]-to-noise ratio or incompletely resolved lines. The uncertainties

reflect a **20** confidence level. Blended lines were weighted according to their relative intensities.

The Hamiltonian is schematically described by

$$\mathcal{H} = \mathcal{H}_{rot} + \mathcal{H}_{hfs}$$

The rotational Hamiltonian is a Watson S reduction[21] in the 1' representation[22] and contains centrifugal distortion effects of up to eighths order, The hyperfine Hamiltonian includes nuclear Br quadrupole and spin-rotation effects as well as distortion terms for the diagonal quadrupole constants of the form $[(\chi_J P^2 + \chi_K P_z^2), \mathcal{H}_Q]$. All operators arc defined positively, except D_J, D_{JK}, and D_K for reasons of tradition.

Values for each of the rotational constants arc very similar among the isotopomers. l'bus, it can bc expected that the distortion constants arc quite similar as we] 1, 1 lowever, some of the higher order constants showed initially isotopic variations much larger than expected. in order to extract the most information from the data set the spectroscopic constants were determined in a single, global, non-linear least-squares fit. A set of common constants was used for H_J, h_1, and the oct ic constants used in the fit. Some higher order constants C (d_2 and the remaining diagonal sextic constants) were constrained so that

$$C(81) = 2C(79,81) - C'(79)$$

This relationship is quite good even when sufficient data is available to dermine all three constants independently.

1 :ach of the hyperfine constants were fixed together for all nuclei using the appropriate i so-topic relationships taken from the Br atom.[23] It should be pointed out that for molecules where the quadrupole constants were determined very precisely, the isotopic ratios arc very c1osc to the atomic

value.[24] Because of the rotation of the principal axis system of the mixed isotopomer with respect to the symmetric ones its quadrupole tensor had to be adjusted. These corrections have been estimated from the structure and the quadrupole constants of the symmetric isotopomers. Corrections were not taken into account for the distortion parameters on the quadrupole constants and for the spin-rotation constants because the effects of the axis rotation for the mixed isotopomer were much smaller than the uncertainties of the respective constants.

The quadrupole constant χ_{aa} was mostly determined by transitions with low J and $K_a \geq 5$ while χ_{-} was mostly determined by transitions with $K_a \leq 4$ and rather high J (see Table 2). This may explain why the J-distortion on χ_{-} and the K-distortion on χ_{aa} were significantly determined. The inclusion of χ_{aa}^{K} in the fit removed systematic deviations between calculated and observed quadrupole splittings at higher K_a's.

initially the $v_2 = 1$ state data was fit separately holding all ground state constants of $^{79}Br_2O^{81}Br$ fixed and fitting those differences which seemed to be appropriate for the current set of transitions. Changes in the rotational and diagonal quartic distortion constants as well as H_K and χ_{aa} were determined. Later the same molecular parameters were used in the combined fit.

Higher order parameters were kept in the fit if they reduced the standard deviation and did not introduce a high degree of correlation among the parameters. Some parameters with rather large uncertainties were retained although their effects on the quality of the fit were small. In such cases the uncertainties may be used to place reasonable limits on the magnitude of such terms and provide more realistic calculations of the uncertainties of other molecular parameters and the positions of unobserved lines. The particular choice of parameters has essentially no effect on the molecular para-

meters derived from the rotational and quartic distortion constants or from the quadrupole tensor. The magnitude from the K-dependent to the *J*-dependent and from the quartic to the octic distortion constants decrease rapidly and in a very regular way indicating that even the less well determined higher order parameters arc of the right order of magnitude,

The spectroscopic constants of the ground and excited vibrational states arc in Tables 111 and 1 V respectivel y. Statistics of the fit arc in '1'able V.

(c) Structural Parameters. The Br_2O ground-state effective (r_o) structure may be calculated from any two of the three moments of inertia or the *a* and *b* planar moments for each of the isotopic species. '1 'able VI gives the r_0 structure determined from a least-squares fit to the planar moments of all three isotopomers. The numbers in parenthesis represent the range of values when different choices of moments were used in the fit, Because the uncertainties of the rotational constants arc very smal 1, the structural parameters determined by either method arc highl y precise and agree among the i sotopomers to more than the quoted figures. The accuracy of the structural parameters is entire] y limited by vibrational effects.

The ground-state average (r_z) structure was calculated from the B_z^g (l'able V]). The harmonic contributions to the a-constants were calculated from the harmonic force field (*vide infra*) and subtracted off of the B_0^g to obtain the ground-state average rotational constants B_z^g (see "1'able VII). Because the inertial defects calculated from the ground state average rotational constants arc smaller by a factor of -40 (ideally it should be zero) than those from the ground state effective constants, structural ambiguities arc reduced by a similar amount. Isotopic differences in the r_z structure arc

very small. For the bond length they are of the order of what can be derive from the formula below.

1 {equilibrium structural parameters can be estimated using an equation proposed by Kuchitsu:[25]

$$r_e = r_z - 3/2\ a\ \langle u^2 \rangle + K.$$

1 lere $\langle u^2 \rangle$ and K arc the zero-point mean square amplitude of the BrO bond and its perpendicular amplitude correction, respectively. The constant a is a Morse anharmonicity parameter,[26] 1.976 $Å^{-1}$, derived from the BrO radical.[17] In this model differences bet wccn ground-state average and equi librium bond angles arc neglected. The estimate of r_e is also in 'l'able VI together with structural data of related compounds. 'I 'o allow a better comparison, the parameters of Cl_2O were calculated as described above for Br_2O using rotational constants of $^{35}Cl_2O$ from Ref. 27, the harmonic force field from Ref. 13, and the Morse anharmonicity parameter 2.201 $Å^{-1}$, of ClO, derived from Ref. 28.

The Br-Br substitution distance can be well dctcrmincd: 305.87 pm, slight] y smaller than the respective r_0 and r_z values, but larger than the r_e value. Because of the small h-coordinate of the Br atoms (-9.47 pm) together with vibrational effects it is difficult to locate the O atom precisely without oxygen substitution.

(d) Harmonic Force Field calculations have been performed for Br_2O to obtain initial centrifugal distortion constants, to calculate a ground-state average structure and to estimate equilibrium structural parameters (*vide supra*), and to gain some insight into the bonding of this molecule. The computation was performed using Christen's NCA program.[29]

The stretching fundamentals have been observed in argon matrices.[8] Whereas neon matrix

wavenumbers usually are very c1osc to gas phase values, those from other matrices can exhibit shifts of up to a few percent. In order to estimate gas phase harmonic wavenumbers, the symmetric and asymmetric stretching frequencies were scaled by 1.005 and 1.014, respective] y. These values were derived from gas phase[27] and argon matrix[30] values for ν_1 and ν_3 of $^{35}Cl_2O$. These estimates of anharmonic gas phase wavenumbers were harmonized as described c]sewhcrc,[31] using $\omega/\nu = 1.020$ which was taken from a recent force field calculation of HOBr.[15b] Since no $^{79,81}Br$ isotopic shifts were resolved, the frequencies were attributed to the $^{79}Br^{16}O^{81}Br$ and $^{79}Br^{18}O^{81}Br$ isotopomers, respective] y, because the mixed isotopomers arc the most abundant ones and their vibrational wavenumbers arc very close to the average of the respective symmetric isotopomers.

Among the different types of input data the weights were chosen to reproduce all the input data in a satisfactory way. The input data were weighted inverse] y to the squares of their attributed uncertainties. A hundred times the experimental values were used for the quartic distortion constants, 1 cm^{-1} and 0.3 cm^{-1} for the vibration] wavenumbers and isotopic shifts, respectively, the experimental uncertainty was used for the V_2 inertial defect difference.

The r_0 structure has been used initially to describe the geometry of the molecule. The resulting force field was used to derive the r_z structure and to estimate the equilibrium structure (*vide supra*). 'l'his r_e structure was used in the final calculation. The resulting force constants with the potential energy distribution (1'1 :D) for the vibrational wavenumbers, results from an *ab initio* calculation, and experimental values for Cl_2O and F_2O are given in Table VII 1. A comparison of the input data with values calculated from the force field arc given in "l'able 1X.

111. DISCXJSS1ON

(a) Structure and Force Field. The present force field reproduces the input data quite well. The differences between ground-state and equilibrium centrifugal distortion constants account for a substantial amount of the residuals (compare for example ground-state distortion constants with those of the excited bending mode, or scc Ref. 15b for the case of DOBr). The residuals of the vibrational wavenumbers and their isotopic shifts may be duc to perturbations in the matrix and the way the gas phase harmonic wavenumbers were approximated.

The solid state EXAFS data agree with the structural parameters of Br_2O in the gas phase within the large EXAFS uncertainties (r = 185 (1) pm, α = 112 (2)°).[9] 1 lowever, a more recent single crystal X-ray diffraction study indicates larger structural differences between the solid and the gaseous states; two non-equivalent bonds of 185.7 (5) and 187.5 (5) pm and an angle of 114.2 (2)" were found, [10]

The structural parameters and force constants of Br_2O agree reasonabl y well with those from a high level *ab initio* calculation.[32] The overestimation of the bond length and the underestimation of the stretching force constants arc fairly common for this type of calculation.

The estimated equilibrium structural parameters of Cl_2O, derived from the ground-state average structure as described above, agree very well with those derived from equilibrium rotational constants (SCC'1 'able V]). The agreement is even better, when the latter is calculated from P_a and P_b. The small differences arise from the fact that the experimental equilibrium inertial defect is slightly different from zero. Thus it seems reasonable to assume that the estimate of the Br_2O equilibrium structure

is a good one too.

'J'here is an apparent trend in the force constants of X_2O compounds, and the differences in the diagonal force constants between F_2O and Cl_2O are much larger than those between Cl_2O and Br_2O, as expected. The stretching force constants f_r of Br_2O and Cl_2O are very similar; this may be related to the essentially pure single bond character of the XO bonds in these molecules.

The BrO bond in Br_2O is slightly larger than in HOBr, the situation is very similar for the ClO bonds in Cl_2O and HOCl. The increasing size of the X atom corresponds with an increasing bond angle in X_2O and 1 I OX (X = Cl, Br).

(b) Hyperfine Constants. The three independent parameters which describe the Br quadrupole tensor of Br_2O completely, χ_{aa}, χ_{-}, and χ_{ab}, could be determined quite well, particularly in the global fit. Consequently, it has been possible to determine the orientation of the principal quadrupole axes with respect to the BrO bond. The z-axis of the quadrupole tensor is tilted 2.4" away from the BrO bond toward the other Br atom as shown in Fig. 6. The situation is quite similar to that reported recently for Cl_2O.[13] Although care is advised when ground- and excited-state quadrupole constants arc combined, it is likely that the general conclusions for Cl_2O arc not seriously affcctcd, because vibrational effects on these constants arc expected to be small with respect to the uncertainties.

From the principal components of the quadrupole tensor onc can calculate the ionic, i_c, and n-characters, π_c of the XO bond in Br_2O and Cl_2O.[19, 22] The results arc shown in l'able X together with those of related compounds. 1 3oth X_2O molecules have essential] y covalent XO bonds with almost negligible contributions from π-back bonding. '1 'he ionic characters derived in this way arc

in line with the view that the XO group (X = halogen) is only slightly more and the Br atom less electronegative than the Cl atom.

It should be noted that in the absence of a good measurement of χ_{ab} the usual assumption that the *z*-quadrupole axis coincides with the chemical bond would lead to a significant error in the calculation of χ_z and χ_x. For a nearly cylindrical y symmetric bond

$$\frac{\Delta\chi_x}{\chi_x} \approx \frac{2\Delta\chi_x}{\Delta\chi_x} \approx \frac{3\cos 2\theta_{za}}{2\cos 2\theta_{ra}}$$

where θ_{za} is the angle between the z- and the a-axis and θ_{ra} is the angle between the bond and the *a*-principal axis. "l'he A's refer to the errors introduced in the respective constants. For the present case $\Delta\chi_x/\chi_x \approx 30940$ and $\Delta\chi_z/\chi_z \approx 15\%$. For Cl_2O these errors lead to estimates of the ionic and n-contributions of 0.35 and 0.08 respectively.[16] Similarly onc would derive values of 0.48 and 0.12 for Br_2O. It is noteworthy that in both cases the n-electrons would be in the molecular plane, increasing the ionic character duc to the o-bond. These ionic characters arc larger than those of ClF and BrF respectively, scc '1'able X. 'his is rather unusual considering that fluorine is the most electronegative element and the fact that the ionic character of a given bond should depend on the electronegativity of the atoms or atom groups involved.

Two quadruple distortion terms have been determined significantly. For a rather rigid molecule one would expect the ratios χ_{aa}^{K}/χ_{aa} and χ_{-}^{J}/χ_{-} to be of the order of $-D_K/A$ and $4\,d_1/(B-C)$. Thus χ_{aa}^{K} and χ_{-}^{J} should be of the order of-17.5 and -0.58 kHz, respectively, for the ^{79}Br nucleus, close 10 the experimental values of-29.4 (26) and -0.520 (94) kHz.

In contrast to the quadrupole coupling constants, the spin-rotation coupling constants of Br_2O are not particularly well determined. The spin-rotation constants of Br_2O can be used to estimate the paramagnetic shielding $\sigma_p^{(Br)}$ at the Br nucleus:[37] *ca.* -3650 ppm; because of the relatively large uncertainties of the spin-rotation constants that value has to be viewed tautiously. The absolute value is close to that of BrF (*cu.* **-3700** ppm)[24] and BrNO (*ca.* -3770 ppm),[38] somewhat larger than that of ^{81}IBr (ea. -2490 ppm),[34] but much larger than that of ^{81}IBr (-513 ppm).[39] Thus, it can be concluded that the spin-rotation coupling constants of Br_2O obtained in this study are of the right order of magnitude.

IV. CONCLUSION

The first high resolution study of Br_2O has been performed in the millimeter and submillimeter regions. Precise spectroscopic constants have been obtained for $^{79}Br_2O$, $^{79}BrO^{81}Br$, and $^{81}Br_2O$ in the ground vibrational states and for the mixed isotopomer in the first excited bending mode permitting structural parameters and the harmonic force field to be determined. It has been shown that the determination of the off-diagonal quadrupole coupling constant χ_{ab} is crucial to diagonalize the quadrupole tensor properly and to derive ionic and n-contributions.

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TABLE I: Rotational transitions' of Br_2O used in the fits.

	ground state			$\nu_2 = 1$
	$^{79}Br_2O$	$^{79}BrO^{81}Br$	$^{81}Br_2O$	$^{79}BrO^{81}Br$
$^{r}Q_0$		56		
$^{p}R_1$	39		40	
$^{r}Q_1$	19^{l}	19^{l}		
$^{r}R_2$	78U	55", 79^{u}	80^{u}	
$^{r}P_2$		26^{u}		
$^{r}R_3$	$34^{l,u}$, 60^{U}, 61 ', 62^{1}, 69u	$35^{l,u}$, 601', 62^{U}, 63^{l}, 64^{1},791	351'",621>",631',641, 71 ", 75", 77', 80', 87^{1}	$33^{l,u}$, 34^{1},351, 36^{l}
$^{r}R_4$	45^{U}, 46^{1},471'",481'" 51'"", $53^{l,u}$ '	$46^{l,u}$, 47^{1},481'", ^{4}91, 51', 54'""	$47^{l,u}$, $48^{l,u}$, $49^{l,u}$) $54^{l,u}$, 55'	471>11,481>11, 53^{u}
$^{r}R_5$	23,27-30	27-30, $64^{l,u}$	14,23,24,24,28-31	25,27,28
$^{r}R_6$	6	6,40	6	
$^{r}Q_6$	25, 34-37,40,45-59, 87", 88^{1}, 911'", 93", 111', 112', 1141'1', 1161, 1181, 121', 123"	29,30,37,38,50-52, 59, 60, $84^{l,u}$, 1121,1131,1141', 115", 1161'", 1171, 119", 120", 121^{l}	7-14,16-24,28-41, 105^{1}, 1061, 1081', 110^{l},111^{u}, $112^{l,u}$, 115', $117^{l,u}$,119"1', 120', 121^{u}	45,47,52,54,55, 57
$^{r}P_6$	36	36,38	37	36
$^{r}P_7$	21,24,32,61	24,33,60	19,33,61,62	62,63
$^{r}P_8$	40,41,47,48,57	40-42,47-49	41,42,49,58	43-46,50
$^{r}P_9$	64,72,80,81,82	65,66,71,77,82, 83	65,66,71-73,82-84	67,72,73
$^{r}P_{10}$	92,93	54, 89,90,97	90,91,98	
$^{r}P_{11}$		121		

[a] in symmetric top notation. [l,u] Lower and upper KC, respectively, of the lower state.

TABLE 11: Observed frequencies (Ml lz) and assignments' of selected rotational transitions with large quadrupole splittings, uncertainties[b] (kHz), and residuals (kHz) (o-c) of Br_2O.

Isotopomer $J_{Ka,Kc}$ - $J''_{Ka',Kc'}$		C	
1,1"- I',I'	ohs. freq.	uric.	o-c
$^{81}Br_2O$	156, -145,	χ_{aa}	
3,16-3,15	388795.566	50	24
0,15-0,14	388796.813	120	36
3,15-3,14	388797.263	120	-26
1,14-1,13	388798.278	50	-21
2,13 -'2,12	388807,580	50	-16
2,14-2,13			
2,16-2,15			
3,14-3,13			
1,16-1,15			
2,17-2,16			
3,13-3,12	388810.769	70	3
3,18-3,17	388816.909	80	29
2,15-2,14	388818.222	60	-13
1,15-1,14			
3,12-3,11	388819.749	80	-42
$^{81}Br_2O$	$^{7}7,$ - $6_{6,}$	Xaa	
3,5 -3,4	431048.334	100	-32
3,7 -3,6	431049.319	80	-30
1,6- 1,5	431051.593	50	-2
3,6- 3,5	431055.045	80	28
0,7- 0,6			
3,8 -3,7	431056.731	60	-11
1,8- 1,7	431059.165	100	-5
3,4 -3,3	431060.802	60	38
2,5 -2,4			

2,6- 2,5			
2,9- 2,8			
2,8- 2,7			
1,7- 1,6	431066,426	70	-58
2,7 -2,6			
3,9- 3,8	431067.341	100	21
3,10 -3,9	431070.3	50	-6
$^{79}Br_2O$	$40._{,40}$ -39,,39	x-	
2,40-0,39	90757.144	25	12
2,41-2,40	90781.817	25	-12
2,42-2,41	90783.336	25	-5
2,39-2,38			
2,38-2,37			
0,40-2,39	90808.148	40	7
$^{81}Br_2O$	^{41} 0,41-401,40	x-	
3,42-3,41	90859.569	20	7
3,41-3,40	90859.938	30	*-4*
3,40-3,39	90860.260	30	*14*
3,43-3,42	90878.834	30	14
1,42-1,41	90880,650	30	-12
1,40-1,39	90881.669	30	-o
3,39-3,38	90882.424	30	-14
3,44-3,43	90900.97s	40	-15
1,41-1,40	90902.422	30	-8
3,38-3,37	90903.897	30	-12
^{79,R}111r20	$79_{4,76}$ - $78_{3,75}$	χ_{-}, (χ_{ab})	
	$77_{4,73}$ - $78_{3,75}$ = 4063 MHz		
3,82-3,81	418562.770	300	96
1,79-1,78	418563.295	90	-1oo
0,79-2,78			

3,76-3,75	418563.838	200	-233
1,80-1,79	418579.500	100	117
3,77-3,76			
2,81-2,80	418581.041	75	-82.
1,78-2,77			
2,80-2,79	418582.500	150	-56
3,81-3,80	418583.497	70	68
2,77-2,76			
2,78-1,77	418584.647	60	1
3,78-3,77	418598.881	80	-74
3,80-3,79	418601.998	60	11

$^{79/81}Br_2O$ $80_{3,77\text{-}792>78}$ χ_{-}, χ_{ab}

$80_{3,77\text{-}794,75}$ = 2732 MHz

3,79-3,78	412123.002	80	22
3,80-3,79	412124,194	150	-18
2,78-2,77	412168.595	80	-10
2,79-2,78	412169,412	80	6
1,81-1,80	412173.000	60	22
3,82-2,81	412174.249	60	-30
1,79-1,78	412178.295	50	-15
3,77-3,76	412222.086	50	-2

$^{79}Br_2O$ 525,47-514,48 χ_{ab}

$54_{4,51} - 52_{5,47}$ = 417 MHz

2,51-2,50	425858.447	80	-24
2,54-2,53	425865.497	70	22
2,53-2,52	425874.634	60	-13
0,52-0,51	425877.021	65	-14
2,52-2,51	425885.018	75	16
2,50-2,49	425897.373	70	21

$^{81}Br_2O$	565,52-554,5,	χ_{ab}	
	$53_{5,49} - 55_{4,51}$= 874 MHz		
3,59-3,58	432454.813	400	-71
3,58-3,57	432455.846	150	60
1,55-1,54			
1,57-1,56			
3,57-3,56			
1,56-1,55	432459.612	90	-11
3,56-3,55	432461,986	120	26
3,53-3,52	432464.130	120	29
3,54-3,53	432466.154	120	5

[a] For blended lines frequencies, uncertainties an residuals arc given only for the first hyperfine components, only *I* and *F* assignments for the remaining components. Components not observed or not used in the fit have been omitted. For transitions affected by χ_{ab} the the perturbing levels and energy differences arc also given.

[b] 20 confidence level.

TABLE III: Spectroscopic constants' (MI Iz) and inertial defect (amu Å^2) of Br_2O in the ground vibrational state.

	$^{79}Br_2O$	$^{79}BrO^{81}Br$	$^{81}Br_2O$
Rotational constants			
$A - (B+C)/2$	31879.7770 (66)	31857.985 S (48)	31836.1153 (79)
$(B+C)/2$	1340.84020 (33)	1324,56744 (28)	1308.32641 (42)
$(B-C)/4$	13.732064 (48)	13.416095 (32)	13.104093 (46)
A	*33220.6172 (64)*	33182.5530 (47)	33144.4417 (76)
B	*1368.30433 (29)*	1351.39963 (30)	1334.53459 (36)
C	*1313.37607 (39)*	1297.73525 (28)	1282.11822 (48)
Inertial defect			
A^2	*0.234085 (1 87)*	0.234149 (163)	0,234195 (246)
Quartic centrifugal distortion constants			
$D_J \cdot 10^4$	*2.85030 (82)*	2.78410 (80)	2.71842 (90)
$D_{JK} \cdot 102$	-1.913650 (264)	-1.891064 (238)	-1.868525 (231)
D_K	1.051 317(126)	1.048704 (96)	1.046052 (151)
$d_1 \cdot 10^5$	-1.96723 (124)	-1.90199 (119)	-1.83822(121)
d_2 " 10^7	-3.5330 (291)	-3.3658 (151)	-3.1986(291)
Sextic centrifugal distortion constants			
$H_J \cdot 10^{11}$	6.84 (60)	6.84 (60)	6.84 (60)
H_{JK} " 10^9	4.487 (167)	4,422 (159)	4.356 (167)
$H_{KJ} \cdot 106$	-2.535 (41)	-2.493 (38)	-2.450 (41)
H_K " 10^4	1.1680(109)	1.1622(103)	1.1564(109)
h_1 " $10^{1'}$	1.793 (99)	1.793 (99)	1.793 (99)
Octic centrifugal distortion constants			
L_{JK} " 10^{12}	-6.59 (1 69)	-6.59 (169)	-6.59 (169)
L_{KKJ} " 10^{10}	7.34 (1 92)	7,34 (192)	7.34 (192)
$l_K \cdot 10^*$	-2.62 (47)	-2.62 (47)	-2.62 (47)

Nuclear quadruple coupling constants and quartic distortion terms[c]			
χ_{aa}	551.119(196)	-0.987 0.821	461,232 (164)
$\chi_{aa}^{J} \times 10^{4}$	2.0 (21)		1,7(18)
$\chi_{aa}^{K} \cdot 10^{2}$	**-2.93 (20)**		-2.45 (17)
x-	**405.361 (208)**	**0.995** **-0.814**	338.633 (174)
$\chi_{-}^{J} \times 10^{4}$	-5.20 (94)		-4.34 (79)
x-K " 10	**1.5 (23)**		1.2(19)
$\|\chi_{ab}\|$[d]	**613.112(333)**	**0.503** **0,422**	512.185 (279)
Nuclear spin-rotation constants'			
$C_{aa} \cdot 103$	42.1 (63)		45.3 (67)
$C_{bb} \cdot 10^{3}$	8.4 (24)		9.1 (26)
$C_{cc} \cdot 103$	11.3 **(26)**		12.2 (28)

[a] Numbers in parentheses are two standard deviations in units of the least significant figures. Watson's S reduction was used in the reprensation 1'.

[b] One common constant for all three isotopomers was used for each of H_J, h_j, L_{JK}, L_{KKJ}, and L_K; d_2, H_{JK}, H_{KJ}, and H_K Were constrained so that $C(81) = 2\,C(79,81) - C(79)$; scc text.

[c] Upper (lower) values for ^{79}Br (^{81}Br)nucleus of $^{79}Br_2O$ ($^{81}Br_2O$), isotopic ratios fixed. Values for $^{79}BrO^{81}Br$ arc differences from the values of the respective nucleus for the symmetric isotopomer due to the rotation of the principal axis system; scc also text.

[d] $\mathrm{sig}\{\chi_{ab}(Br_1)\} = -\mathrm{sig}\{\chi_{ab}(Br_2)\}$; $\mathrm{sig}(\Delta\{\chi_{ab}(Br_1)\}) = \mathrm{sig}(\Delta\{\chi_{ab}(Br_2)\})$

TABI .E IV: Spectroscopic constants (MI Iz) and inertial defekt (amu Å^2) of $^{79}BrO^{81}Br$ in the first excited bending mode.[a]

parameter	$\nu_2 = 1$	$(\nu_2 = 1) - \nu_0$
Rotational constants		
A -(B+- *C*)/2	32084.7968 (161)	226.8113 (164)
(*B* + *C*)/2	1323,51311 (82)	-1.05433 (85)
(*B* - *C*)/4	13,47581 (114)	0.059 72(1 14)
A	33408.3099 (154)	225.7570 (1 56)
B	1350.46473 (198)	-0.934 89(1 96)
C	1296.56149 (280)	-1.17376 (283)
Inertial defect		
Δ_2	0.43073 (136)	0.19658 (137)
[centrifugal distortion constants		
D_J " 104	2.769 70(1 10)	-0.01441 (102)
D_{JK} · 102	-1.899923 (318)	-0.008859 (1 89)
D_K	1.092927 (289)	0.044223 (284)
H_K " 104	1,2379 (168)	0.0757 (137)
Qu		

'I'AlI] .E V: Statistics of the fit.

	ground state			$\nu_2 = 1$
	$^{79}Br_2O$	$^{79/81}Br_2O$	$^{81}Br_2O$	$^{79/81}Br_2O$
total number of observed rotational transitions	76	72	96	30
total number of observed lines	156	192	245	76
number of lines with O ≤ residual < 10,	116	141	191	52
1 σ ≤ residual < 2 σ,	30	37	47	17
20< residual < 3 σ,	5	5	6	6
3 σ ≤ residual < 6 σ	5	5	1	1

TABLE VI: Structural parameters (pm, deg) of Br_2O and related compounds.

para-meter	Br_2O[a]				HOBr[b]
	r_0	r_z	r_e[c]	r_e	r_e
r(BrO)	184.29 (20)	184.333 (5)	183.786		182.798
∢(BrOX)	112.24 (20)	112.249 (5)	112.249		102.99

	Cl_2O[d]			[e]	HOCl[f]
r(ClO)	170.13	170.189	169.563	169.59	168.897
<(ClOX)	110.89	110.914	110.914	110.88	102.965

[a] This work, for uncertainties see text. [b] Ref. 15. [c] Estimate from r_z, see text.
[d] This work, rotational constants from Ref. 27. [e] Ref. 13. [f] Ref. 14.

TABLE VII: Ground state average rotational constants (MHz) of Br_2O.

parameter	$^{79}Br_2O$	$^{79}BrO^{81}Br$	$^{81}Br_2O$
A_z	32969,925	32932.482	32894.994
B_z	*1367.0458*	1350.1624	1333.3184
C_z	1312.6012	1296.9699	1281.3624

TABLE VII 1: Force constants ($N\,m^{-1}$) of dihalogen monoxides and potential energy distribution (PED)[a] of Br_2O.

para-meter	Br_2O		Cl_2O	F_2O	PED		
	exptl.[b]	*ab initio*[c]	exptl.[d]	exptl.[e]	ν_1	ν_2	V3
f_r	287.4	253.9	294.9	410.5	0.858	0.084	1.131
f_β	102.3	108.3	123.7	147.1	0.265	0.786	
f_{rr}	33.4	31,6	50.4	86.0	0.100		-0.131
$f_{r\beta}$	28.3	26.6	31.2	22,1	-0,223	0.120	

[a] For $^{79}BrO^{81}Br$; only contributions ≥ 0.03 are given. [b] This work.
[c] CCSD(T)/TZ2P values from Ref. 32 [d] Ref. 13 [e] Ref. 33

TABLE IX: Comparison of experimental spectroscopic constants' (cm^{-1}, kHz, arnu $Å^2$) with those calculated from the force field.

para-	$^{79}Br_2O$		$^{79}BrO^{81}Br$		$^{79}Br^{18}O^{81}Br$		$^{81}Br_2O$	
meter	ohs.	C-o[b]	ohs.	C-o[b]	ohs.	C-oh	ohs.	C-o[b]
$(\Delta)\ \nu_1$		0.90	539.4	-2.3	-26.4	1.31		-0.89
$(\Delta)\ \nu_2$		1.50		177.6		-0.98		-1.51
$(\Delta)\ \nu_3$		0.76	644.7	7.5	-33.0	0.46		-0.77
D_J	0.2850	0.0044	0.2784	0.0010		0.2760	0.2718	-0.0022
D_{JK}	-19.14	-0.45	-18.91	-0.34		-17.01	-18.69	-0.21
D_K	1051	-23	1049	-25		828.9	1046	-25
$10^3\ d_1$	-19.67	-0.34	-19.02	0.01		-20.80	-18.38	0.33
$10^3\ d_2$	-0.353	0.030	-0.337	0.035		-0.366	-0.32	0.038
$\Delta\Delta_2$		0.2025	0.1966	0.0040		0.2259		0.1987

[a] vi for $^{79}BrO^{81}Br$; A ν_i:= $\nu_i(Br_2O)$ - $\nu_i(^{79}BrO^{81}Br)$ eke.

[b] Calculated value minus observed value: equal to the calculated value if no observed value is given.

TABLE X: Quadruple coupling constants and derived parameters of $^{79}Br_2O$ in comparison to related molecules.

parameter	$^{79}Br_2O$[a]	$HO^{79}Br$[b]	$^{79}Br^{35}Cl$[c]	^{79}BrF[d]	$^{35}Cl_2O$	^{35}ClF[e]
χ_{aa} / MHz	552.119 (196)	915.663	875.078	1086.892	-71.45[f]	-145.872
χ_{bb} / MHz	-73.379 (138)	-448.905	-437.539	-543.446	6.86[f]	72.936
$\chi_{cc} \equiv \chi_y$ / MHz	-478.740 (149)	-466.758	-437.539	-543.446	64.59[f]	72.936
$\lvert\chi_{ab}\rvert$ / MHz	613.112(333)	20.4	0	0	–82.[g]	0
χ_z / MHz	927.64 (46)	915.97	875.078	1086.892	-123.2	-145.872
χ_x I MHz	-448.90 (47)	-449.21	-437.539	-543.446	58.6	72.936
η_z	0.03217 (53)	0.0192	0	0	0.05	0
θ_{za} / deg	31.4869 (77)	0.86			32.2[g]	
em / deg	33.87	2.01			34.6[g]	
i_c	0.108	0.109	0.080	0.342	-0.048	0.305
π_c	0.025	0.014			-0.036	

[a] This work. [b] Ref. 34. [c] Ref. 35. [d] Ref. 24. [e] Ref. 36. [f] Ref. 16. [g] Ref. 13.

Figure Captions

FIG. 1: Detail of the $^rQ_6$ branch of $^{79}Br_2O$. Some J assignments are given. The tightening of the quadrupole patterns with increasing J (up to 81) can be seen for J up to 60, when asymmetry splitting becomes prominent; + and - indicate the parity of levels. The band turns at J = 75; the irregular appearance in this region is caused in part by χ_{ab}, and the J assignments of near-degeneracies are also given and indicated by *. See also text and Fig. 4. The P-branch near 414 GHz also belongs to $^{79}Br_2O$.

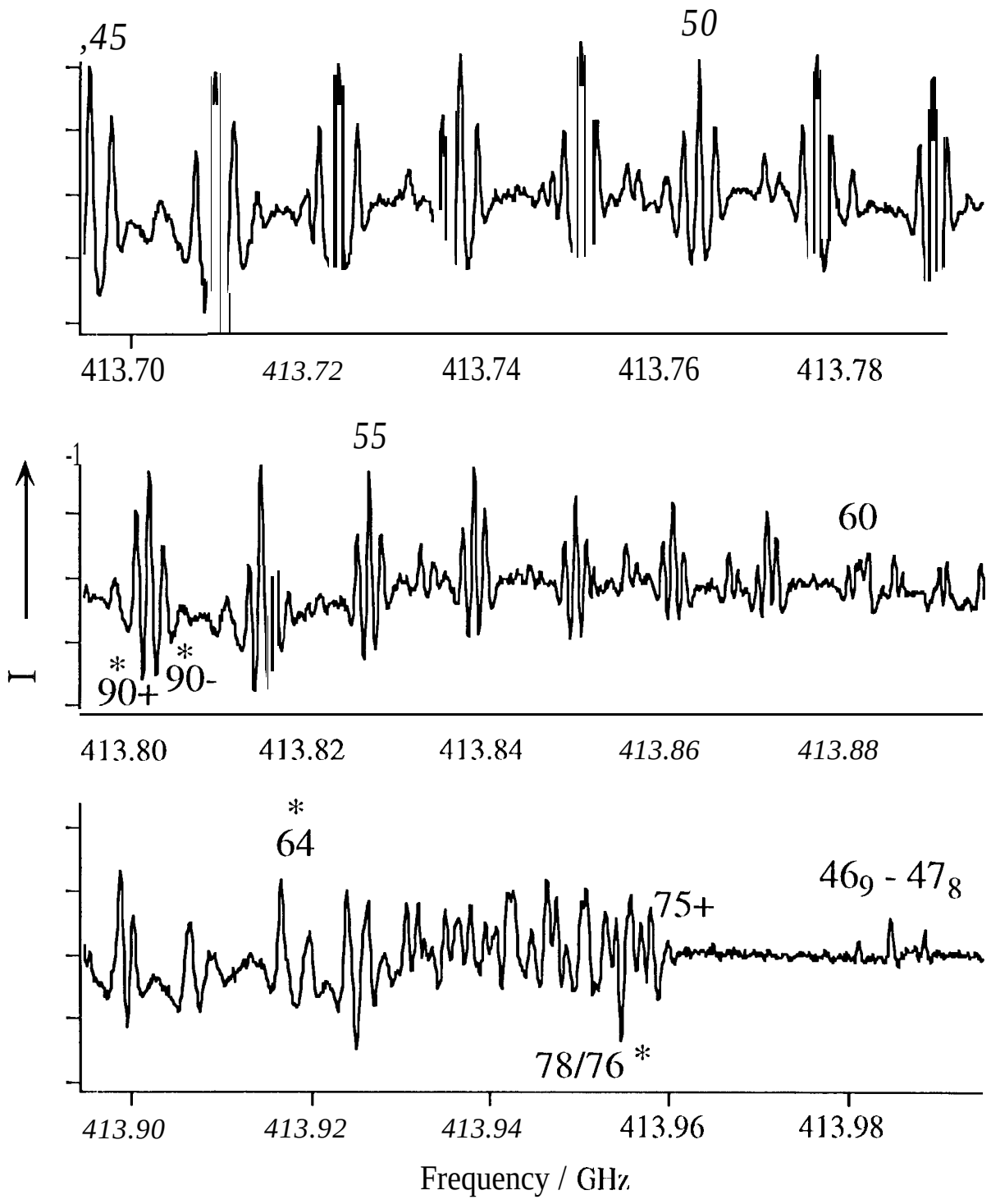
FIG. 2. The $11_{27,\ 105} - 12_{6,\ 106}$ (left) and the $11_{27,\ 106} - 12_{6,107}$ transition of $^{81}Br_2O$ (right) showing quadrupole splittings for high J transitions dominated by χ_{-}. Note: the intensity ratios of *ca.* 1 :4 : 1 and 3 :4:3 are due to the spin-statistics, see text.

FIG. 3: The origin of the K_a = 7-6 R-branch of $^{81}Br_2O$. The hyperfine pattern is dominated by χ_{aa}. The lower state quantum numbers I and F are indicated. Because of the spin-statistics there are only six of 16 strong hyperfine components with $\Delta F = \Delta J$ and I even for the $7_{7,1} - 7_{6,0}$ transition and ten with I odd for $7_{7,0} - 7_{6,1}$.

FIG. 4: The $56_{5,52} - 55_{4,51}$ transition of $^{81}Br_2O$; a) expected pattern without χ_{ab}, b) observed pattern, c) simulated spectrum with χ_{ab}. The energy difference between the unperturbed $53_{5,49}$ and $55_{4,51}$ levels is 874 MHz.

FIG. 5: Near-degeneracies of $^{79/81}Br_2O$. J of the larger K_a value *versus* the absolute value of $\Delta J = 2$, $\Delta K_a = -1$ energy difference is shown. Near-degeneracies accessed by transitions of $^{79/81}Br_2O$ included in the fit are indicated by open circles. Measurable effects are encountered several J's away from the value associated with the smallest energy difference; see also text.

FIG. 6. The principal inertial (dashed arrows) and quadruple axis systems (solid arrows) of Br_2O (c= y is perpendicular to the molecular plane).


,45
50
413.70
413.72
413.74
413.76
413.78
55
-1
60
*
90+
*
90-
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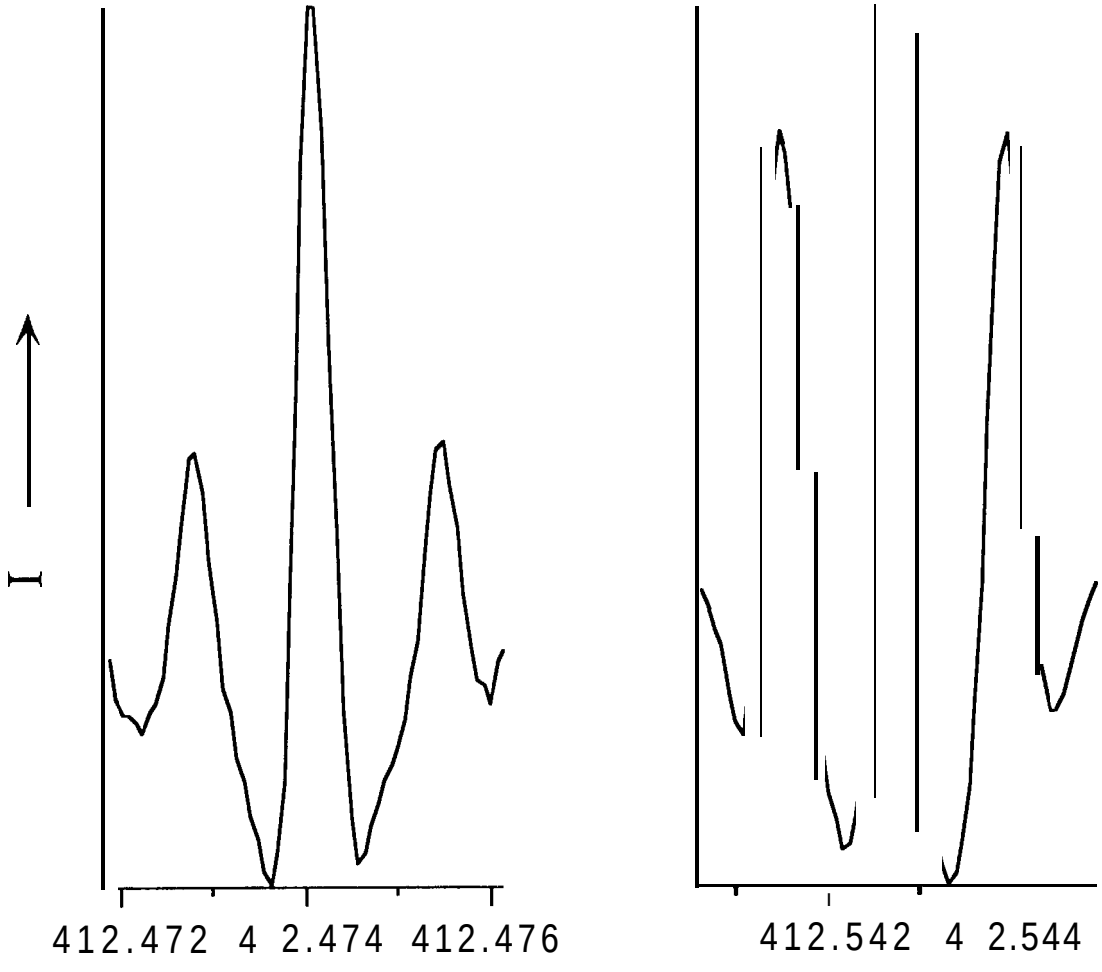
413.80
413.82
413.84
413.86
413.88
*
64
46_9 - 47_8
75+
78/76 *
413.90
413.92
413.94
413.96
413.98
Frequency / GHz


I
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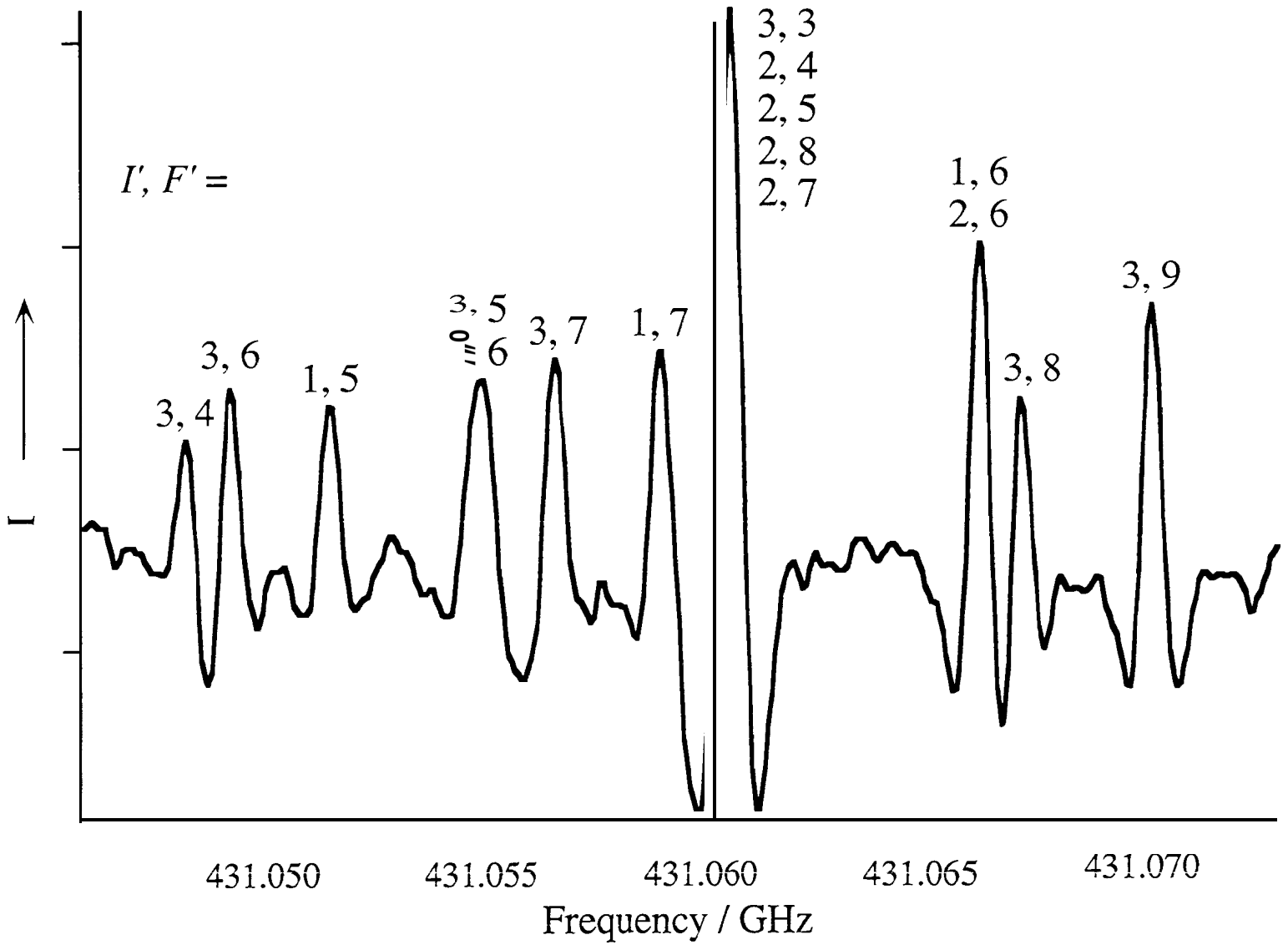
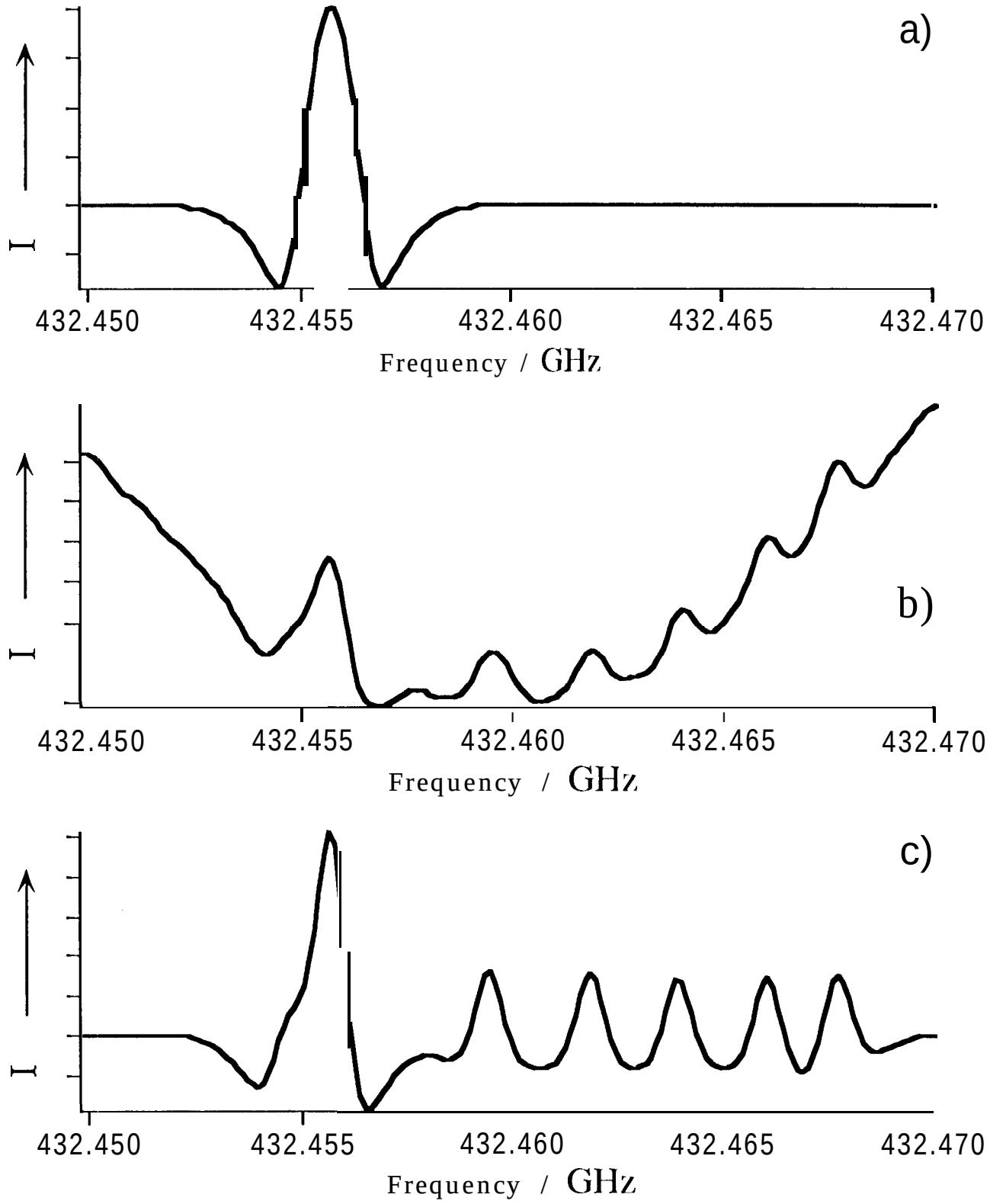
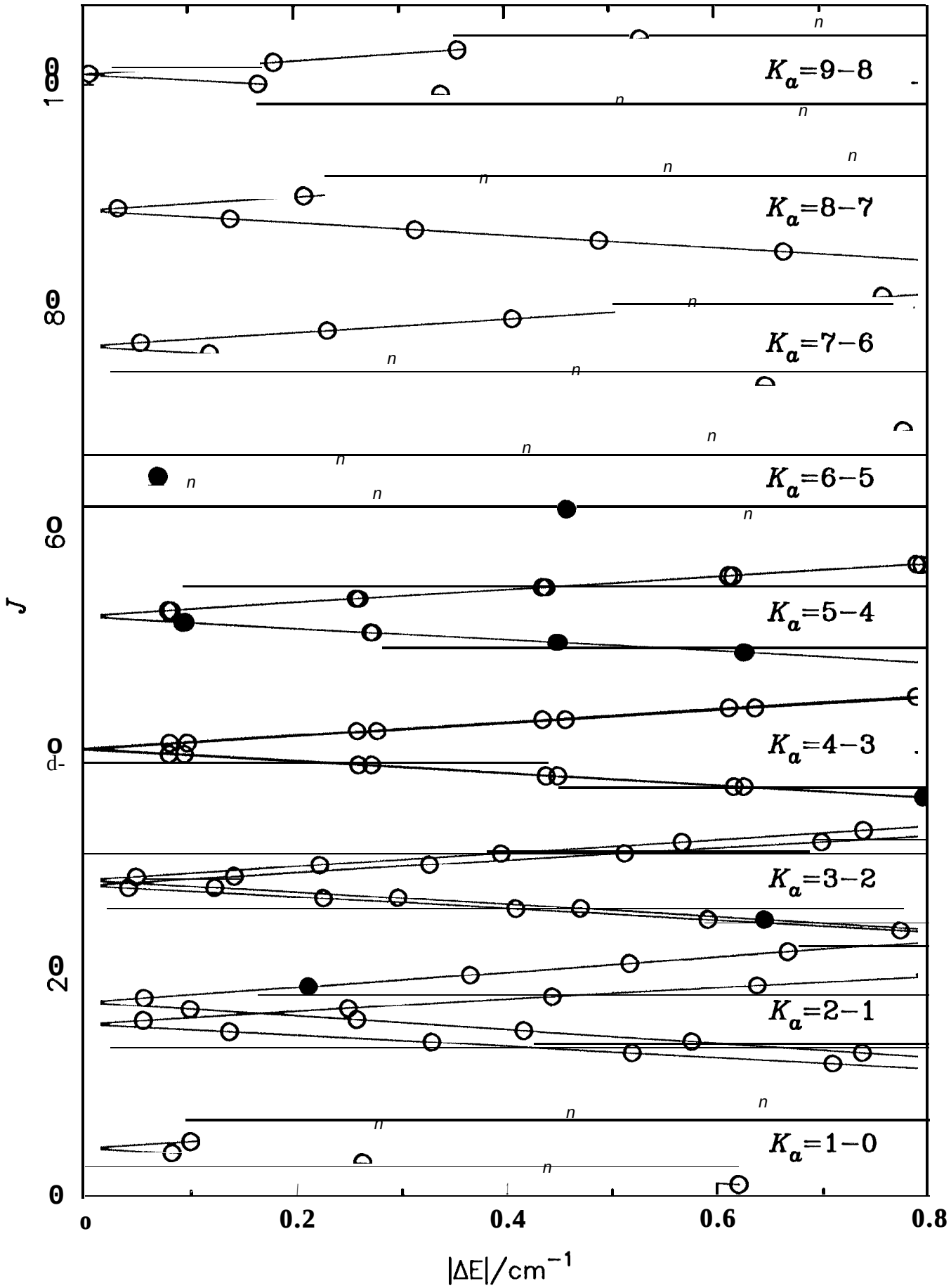
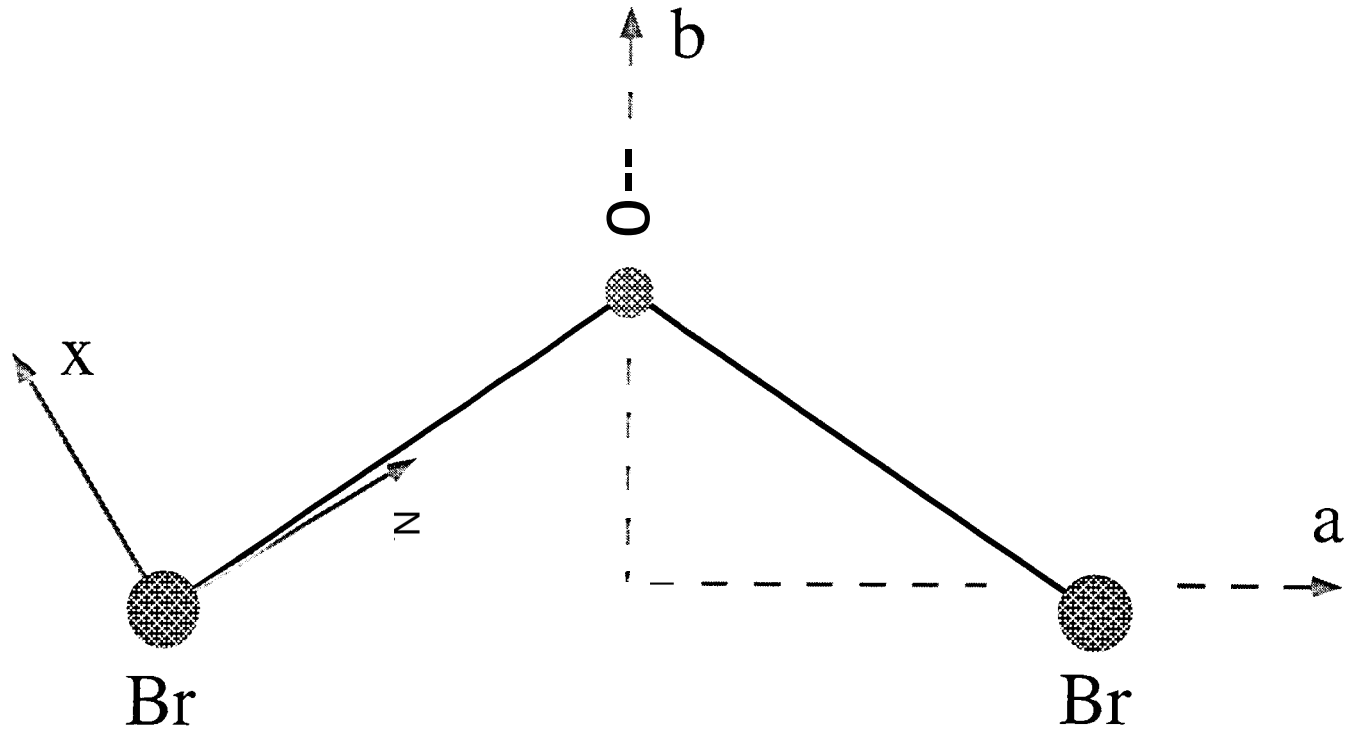
412.542 4 2.544
Frequency / GHz


I′, F′ =
3, 3
2, 4
2, 5
2, 8
2, 7
1, 6
2, 6
3, 9
3, 8
3, 7
1, 7
3, 6
1, 5
3, 4
I
431.050
431.055
431.060
431.065
431.070
Frequency / GHz


a)
I
432.450
432.455
432.460
432.465
432.470
Frequency / GHz
b)
I
432.450
432.455
432.460
432.465
432.470
Frequency / GHz
c)
I
432.450
432.455
432.460
432.465
432.470
Frequency / GHz

J *vs* $\Delta J=2, \Delta K_a=-1$ Intervals




b
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